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(54) Title: SINTER-HOMOGENIZED HEATING PRODUCTS

(57) Abstract

Electrical heating elements operable at high temperatures for long periods are produced by a method involving micropyretic synthesis. Compositions subjected to micropyretic synthesis comprise a powdery mass of electrically conductive and semiconductive material, a reactive system, a grain growth inhibitor and a plasticizer or extrusion agent.

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SINTER-HOMOGENIZED HEATING PRODUCTS

Field of Invention

This invention relates to composite silicide or carbide heating element compositions which include improved combustion sources and refractory silicides such as tungsten silicide. This invention will enable combustion synthesized composite heating elements which include the combustion sources disclosed herein to be used at temperatures up to 1900°C for long periods of time in oxidizing atmospheres.

Background of the Invention

This invention has been conceived to create heating elements which can work at high temperatures for long periods. Accordingly, this invention discloses new micropyretic sources and their combinations which allow for the first time, manufacture of heating elements displaying extended life at very high temperatures. A micropyretic synthesis method is used for the manufacture of heating elements, similar to that disclosed in our co-pending United States patent application 08/027,710, filed March 8, 1993 (herein after referred to as "the '710 application", the contents of which are incorporated herein by way of reference). The synthesis method used in this invention differs from that disclosed in co-pending United States patent application 07/847,782, filed March 5, 1992 (hereinafter referred to as "the '782 application", the contents of which are incorporated herein purely by way of reference), in an important aspect. As in the '782 application, a combustible slurry is prepared, extruded and combusted. However, unlike the '782 application, after combustion, these wire or other shapes are densified and homogenized by passing current, as described in the '710 application.

The '782 application discloses various combustion sources as part of the compositions, for the manufacture of heating elements. $MoSi_2$ composites are preferred in the '782 application. $MoSi_2$ composites are very sensitive to phase composition and impurity at temperatures above 1600°C. The present compositions comprise new undisclosed combustion sources, grain growth inhibitors and other additives which substantially improve the applicability of heating elements manufactured using these compositions at temperatures up to 1900°C. Additionally, some of the combustion sources and their products described in the '782 application may react with filler materials, and therefore may not be suitable as combustion sources for high temperature applications although they may be excellent for low and middle temperature applications (up to 1400°C). The compositions of the present invention are designed so that the combustibles do not react with the silicides, which is believed to be one of reasons leading to the effective utilization of heating elements manufactured using the compositions of the present invention for extended periods at high temperatures. By utilizing combustibles which may react with the filler materials, the '782 application teaches away from the present invention.

The high temperature superiority of heating elements manufactured using the compositions of the present invention, over the compositions of the '782 application, has been observed by experimentation. These experiments have revealed that heating elements using the compositions of the present invention are stable at temperatures above 1400°C, for much longer periods than those manufactured using the compositions of the '782 application. Without exception, a difference in time periods of at least two orders of magnitude has been observed. At temperatures above 1400°C to 1600°C, after operation for 10-100 hours, heating elements using the '782 compositions deteriorate substantially. Conversely, typical heating elements using the compositions of the present invention show similar deterioration at 1400°C to 1600°C, only after 5000 hours.

Additionally, above 1600°C, heating elements using the '782 compositions last for less than 1 hour, whereas typical heating elements using the compositions of the present invention last for greater than 1000 hours. This tremendous increase in high temperature operability, is very beneficial and also quite unexpected.

Summary of the Invention

It is a primary object of the present invention to provide new combustion sources and compositions for manufacturing heating elements which are stable up to 1900°C.

It is a further object of the present invention to provide new combustion sources which will enhance the working temperature and life of heating elements and improve the oxidation resistance of heating elements at high temperatures.

It is another object of the present invention to provide new combustion sources which will prevent any possible reaction between the combustion sources, the combustion products, the silicides and the plasticizers.

It is yet another object of this invention to provide combustion synthesis product(s) with increased creep resistance and strength, by forming in situ compounds between carbides such as tungsten carbide and metalloids such as carbon or silicon. Such compounds are finely and homogeneously distributed in matrix of a major silicide phase e.g. in $MoSi_2$ or WSi_2. In addition, these finely distributed particles will also act as grain growth inhibitors and also influence the recrystallization behavior.

In accordance with the present invention, there is provided a pliable composition comprising by weight percent: (a) between about 10 and 90%

of a powdery mass of electrically conductive and/or semiconductive material selected from the group consisting of WSi_2, $MoSi_2$ and mixtures thereof; (b) between about 5% and 50% of a combustible source which is selected from the group consisting of WO_3 + Al + Si, MoO_3 + Zr + Si, WO_3 + Zr + Si, WC + Si, Mo_2C +Si and mixtures thereof; (c) between about 0.5 to 10% of grain growth inhibitors selected from the group consisting of TiB_2, HfB_2, SiC and mixtures thereof; (d) at least about 1 weight percent bentonite; and (e) at least about 3ml per 30g of the above listed components, of colloidal silica solution.

In accordance with another aspect of the present invention there is provided a method of manufacturing a composite article using the composition described above, comprising the steps of: (a) premixing the powders comprising the combustible source in the composition; (b) blending said premixture with the other components of the composition; (c) forming a pliable slurry from said blend; (d) fashioning said slurry into a final desired article shape; (e) combusting said shape by ignition at a temperature between about 100°C and 1600°C; (f) initially applying sufficient current to said article so as to raise the temperature of said article to a minimum of 50% of the melting point in degrees Kelvin, of the lowest melting phase in the article, wherein the current applied is selected from the group consisting of a DC current, an AC current, a pulsed current and an induction current; and (g) greatly reducing the porosity of said article so as to make the repetitive distance between consecutive homogenous sections of said article to less than 0.002 m, by increasing said current applied so as to cause the elimination of thermal and mass gradients.

In accordance with a further aspect of the present invention, there is provided a pliable composition comprising by weight percent: (a) between about 60 and 85% of a powdery mass of electrically conductive and/or semiconductive material selected from the group consisting of

WSi_2, $MoSi_2$ and mixtures thereof; (b) about 15% of WO_3 + Al + Si as a combustible source; (c) about 2% of HfB_2 as a grain growth inhibitor; (d) about 1 weight percent bentonite; (e) about 3ml per 30g of the above listed components, of colloidal silica solution; and (f) about 0.5 weight percent C.

Detailed Description of the Preferred Embodiment

Examples of specific compositions which have been found to provide heating elements having longer working life up to 1900°C, are disclosed as follows:

Composition 1 (all compositions herein are by weight percent of the total composition, unless otherwise indicated)

WSi_2		10
$MoSi_2$	71.5	
WO_3+ 2Al + 2Si_2		15
HfB_2		2
C (present in the form of graphite in all compositions herein)		0.5
Bentonite		1
Colloidal Silica (type 830 Nycol corporation)		3ml/30g powder (this implies 3 ml per 30g of the remaining components)

Composition 2

WSi_2		20
$MoSi_2$	61.5	
WO_3+ 2Al+ 2Si_2		15
HfB_2		2
C		0.5
Bentonite		1
Colloidal Silica		3ml/30g powder

Composition 3

WSi_2	30
$MoSi_2$	51.5
WO_3+ 2Al + $2Si_2$	15
HfB_2	2
C	0.5
Bentonite	1
Colloidal Silica	3ml/30g powder

Composition 4

WSi_2	40
$MoSi_2$	41.5
WO_3+ 2Al + $2Si_2$	15
HfB_2	2
C	0.5
Bentonite	1
Colloidal Silica	3ml/30g powder

Composition 5

WSi_2	50
$MoSi_2$	31.5
WO_3+ 2Al + $2Si_2$	15
HfB_2	2
C	0.5
Bentonite	1
Colloidal Silica	3ml/30g powder

Composition 6

WSi_2	20
$MoSi_2$	61.5
WO_3+ 2Al + $2Si_2$	7
$2WO_3$+ 3Zr + 4Si	8
HfB_2	2
C	0.5
Bentonite	1
Colloidal Silica	3ml/30g powder

Composition 7

WSi_2	20
$MoSi_2$	57
WO_3+ 2Al+$2Si_2$	5
WC + 3Si	15
TiB_2	2
Bentonite	1
Colloidal Silica	5ml/30g powder

Composition 8

WSi_2	20
$MoSi_2$	54
WO_3+ 2Al+$2Si_2$	8
WC + 3Si	15
TiB_2	2
Bentonite	1
Colloidal Silica	5ml/30g powder

Composition 9

WSi_2	20
$MoSi_2$	52
WO_3+ 2Al+2Si_2	10
WC + 3Si	15
TiB_2	2
Bentonite	1
Colloidal Silica	5ml/30g powder

Composition 10

WSi_2	20
$MoSi_2$	47
WC + 3Si	15
WO_3 + 2Al + 2Si	15
TiB_2	2
Bentonite	1
Water with organic binders	5ml/30g powder.

(organic binders may be methyl cellulose, polyethylene glycol with an average molecular weight. of 200, polyethylene glycol with an average molecular weight of 300, glycerol, 99.5%, polyvinyl butyral, dioctyl adipate and their combinations)

Composition 11

WSi_2	20
$MoSi_2$	57
Mo_2C + 5Si	15
WO_3+ 2Al + 2Si	5
TiB_2	2
Bentonite	1
Colloidal Silica	(5ml/30g powder)

Composition 12

WSi_2	20
$MoSi_2$	54
Mo_2C + 5Si	15
MoO_3+ 2Al + 2Si	8
TiB_2	2
Bentonite	1
Colloidal Silica	5ml/30g powder

Composition 13

WSi_2	20
$MoSi_2$	57
Mo_2C + 5Si	15
WO_3+ 2Al + 2Si	5
HfB_2	2
Bentonite	1
Colloidal Silica	5ml/30g powder

Composition 14

WSi_2	20
$MoSi_2$	47
WC + 3Si	25
WO_3 + 2Al + 2Si	5
TiB_2	2
Bentonite	1
Colloidal Silica	5ml/30g powder

Composition 15

WSi_2	20
$MoSi_2$	47
Mo_2C + 5Si	25
WO_3 + 2Al + 2Si	5
TiB_2	2
Bentonite	1
Colloidal Silica	5ml/30g powder

Composition 16

WSi_2	20
$MoSi_2$	47
Mo_2C + 5Si	25
WO_3 + 2Al + 2Si	5
TiB_2	2
Bentonite	1
Colloidal Silica	5ml/30g powder

Composition 17

$MoSi_2$	87
$2WO_3$ + 3Zr + 4Si	10
TiB_2	2
Bentonite	1
Colloidal Silica	5ml/30g

Composition 18

$MoSi_2$	82
$2WO_3$ + 3Zr + 4Si	5
WO_3 + 2Al + 2Si	10
TiB_2	2
Bentonite	1
Colloidal Silica	5ml/30g

Composition 19

$MoSi_2$	77
$2WO_3 + 3Zr + 4Si$	10
$WO_3 + 2Al + 2Si$	10
TiB_2	2
Bentonite	1
Colloidal Silica	5ml/30g

Composition 20

WSi_2	20
$MoSi_2$	62
$2WO_3 + 3Zr + 4Si$	5
$WC + 3Si$	10
TiB_2	2
Bentonite	1
Colloidal Silica	5ml/30g

Composition 21

$MoSi_2$	87
$2WO_3 + 3Zr + 4Si$	10
Si_3N_4	2
Bentonite	1
Colloidal Silica	5ml/30g

Composition 22

$MoSi_2$	82
$2WO_3 + 3Zr + 4Si$	15
SiC	2
Bentonite	1
Colloidal Silica	5ml/30g

Composition 23

$MoSi_2$	77
$2WO_3 + 3Zr + 4Si$	20
TiB_2	2
Bentonite	1
Colloidal Silica	5ml/30g

Composition 24

$MoSi_2$	77
$2WO_3 + 3Zr + 4Si$	10
$2MO_3 + 3Zr + 4Si$	10
TiB_2	2
Bentonite	1
Colloidal Silica	5ml/30g

Composition 25

WSi_2	10
$MoSi_2$	72
$2MoO_3 + 3Zr + 4Si$	10
WC+3Si	5
TiB_2	2
Bentonite	1
Colloidal Silica	5ml/30g

Broadly stated, the compositions of the present invention comprise between about 10 and 90% of a powdery mass of electrically conductive and/or semiconductive material selected from the group consisting of WSi_2, $MoSi_2$ and mixtures thereof; between about 5% and 50% of a combustible source which is selected from the group consisting of WO_3 + Al + Si, MoO_3 + Zr + Si, WO_3 + Zr + Si, WC + Si, Mo_2C +Si and mixtures thereof; between about 0.5 to 10% of grain growth inhibitors selected from the group consisting of TiB_2, HfB_2, SiC and mixtures

thereof; at least about 1 weight percent bentonite; and at least about 3ml/30g of colloidal silica solution.

The combustion sources have to be premixed before mixing with other powders, in order to produce sufficient heat during combustion. The weight percentage of combustibles in the compositions of the present invention will not be less than 5 wt%, but will not be more than 90%. A combustible content of more than 50% will lead to too strong combustion, and therefore, to samples (heating elements) with large pores and deformed shapes. Compositions with combustibles less then 5% will not be able to produce enough heat to sinter the wire and therefore the wire may not be conductive enough to be finally sintered, densified and homogenized by passing current. The addition of WSi_2 or $MoSi_2$ increases the working temperature, life of heating elements at high temperature and creep resistance, but WSi_2 or $MoSi_2$ content of more than 90 weight percent will drastically decrease thermal shock resistance and oxidation resistance of heating element.

The preferred compositions of the present invention comprise from about 10 to 30 percent WSi_2, up to 4% SiC, up to 3% TiB_2, up to 3% HfB_2 (said SiC, TiB_2 and HfB_2 being at least 0.5 percent), close to 2% bentonite and close to 15ml/100g of powder of colloidal silica. The most preferred composition for manufacturing high temperature heating elements is as follows: 15-30 percent of WSi_2, 15-20 percent combustibles, 1-2 percent TiB_2 and HfB_2 and 0.5-1 percent C. Heating elements made from compositions 1, 2 and 3 above, lasted for over 1000 hours at temperatures from 1700 to 1750°C.

Yet another preferred and unique composition discloses the use of a combination of WC + Si or Mo_2C + Si with WO_3 + Al + Si or WO_3 + Zr + Si. The content of carbide combustion source (WC + Si or Mo_2C + Si) will be from 1 to 50%; oxide combustion source (WO_3 + Al + Si or WO_3

+ Zr + Si) will be 5-30%. The total weight percent of the combustion source is at least 5%. In its more preferred aspects, the carbide combustion source ranges from 15 to 20%, oxide combustion source will be 5-10 wt%. By using carbide combustion sources, alumina content in the final products will be tremendously reduced. It was found that heating elements manufactured using a combination of carbide and oxide combustion sources (for instance, composition 9), show excellent temperature capacity and improved life up to 1850°C.

Yet another preferred and unique composition discloses WO_3 + Zr + Si and MoO_3 + Zr + Si as combustion sources or combinations thereof. These compositions show strong and stable combustion when mixed with $MoSi_2$ and WSi_2 powders. The final products of these combustion sources are WSi_2 (or $MoSi_2$) and ZrO_2. Part of ZrO_2 will react further with SiO_2 during sintering to form zircon which has high melting point and phase stability with $MoSi_2$ and WSi_2. The total weight percent of the combustion source in these compositions is at least 5%. In its more preferred aspects, the WO_3 + Zr + Si combustion source will be from 10 to 25 weight percent. It was found that the compositions using this combustion source show excellent sintering properties and high temperature capability up to 1850°C.

Optimal (these are merely preferred particle sizes) particle sizes are disclosed for various the components listed above as follows:

SiC	-	1µm
WSi_2	-	4µm
Zr	-	3.5-4µm
$MoSi_2$	-	4µm
C	-	-300 (-15µm)
WO_3	-	8µm
Mo_2C	-	-325 mesh (-44µm)
Al	-	-325 mesh (-44µm)

Si	-	-325 mesh (-44μm)
HfB_2	-	-325 mesh (-44μm)
WC	-	1μm
TiB_2	-	1μm
MoO_3	-	8μm
Si_3N_4	-	-325 mesh (-44μm)
Bentonite	-	5μm
Colloidal silica		nanosize colloid

Thus it is apparent that there have been provided, in accordance with the invention, compositions suited for preparing heating elements which may be operated at temperatures up to 1900°C or for very long durations at lower temperatures such as 1750°C, which fully satisfy the objects, aspects and advantages set forth above. While the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description. For example, it is contemplated that in addition to the combustion sources described and claimed herein, a particular composition may comprise other combustion sources. Accordingly, it is intended to embrace all such alternatives, modifications and variations which fall within the spirit and scope of the appended claims.

CLAIMS

1. A pliable composition comprising by weight percent:

   (a) between about 10 and 90% of a powdery mass of electrically conductive and/or semiconductive material selected from the group consisting of WSi_2, $MoSi_2$ and mixtures thereof;

   (b) between about 5% and 50% of a combustible source which is selected from the group consisting of WO_3 + Al + Si, MoO_3 + Zr + Si, WO_3 + Zr + Si, WC + Si, Mo_2C +Si and mixtures thereof;

   (c) between about 0.5 to 10% of grain growth inhibitors selected from the group consisting of TiB_2, HfB_2, SiC and mixtures thereof;

   (d) at least about 1 weight percent bentonite; and

   (e) at least about 3ml per 30g of the above listed components, of colloidal silica solution.

2. The composition of claim 1 further comprising up to 1 weight percent carbon; up to 2 weight percent bentonite; and up to 15ml per 30g of the above listed components, of colloidal silica.

3. The composition of claim 1 further comprising up to 20 weight percent bentonite.

4. A method for the preparation of integral articles having improved mechanical stability, room temperature fracture toughness, and oxidation resistance at temperatures up to 1900°C, and stable electrical conductivity, comprising the steps of:

(a) premixing the powders comprising the combustible source in the composition of claim 1;

(b) blending said premixture with the other components of the composition of claim 1;

(c) forming a pliable slurry from said blend;

(d) fashioning said slurry into a final desired article shape;

(e) combusting said shape by ignition at a temperature between about 100°C and 1600°C;

(f) initially applying sufficient current to said article so as to raise the temperature of said article to a minimum of 50% of the melting point in degrees Kelvin, of the lowest melting phase in the article, wherein the current applied is selected from the group consisting of a DC current, an AC current, a pulsed current and an induction current; and

(g) greatly reducing the porosity of said article so as to make the repetitive distance between consecutive homogenous sections of said article to less than 0.002 m, by increasing said current applied so as to cause the elimination of thermal and mass gradients.

5. An integral article having improved mechanical stability, room temperature fracture toughness, and oxidation resistance at temperatures up to 1900° C, and stable electrical conductivity, produced in accordance with the process of claim 4.

6. An electrical heating element capable of being used at temperatures up to 1900°C formed by micropyretic synthesis of the composition of claim 1.

7. An integral article having improved mechanical stability, room temperature fracture toughness, and oxidation resistance at temperatures up to 1900°C, and stable electrical conductivity, comprising an integral article formed by micropyretic synthesis of the composition of claim 1.

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8. An electrical heating element suitable for use as a high temperature indicator comprising an integral article formed by micropyretic synthesis of the composition of claim 3.

9. An electrical heating element capable of being used at temperatures up to 1900°C comprising an integral article formed by micropyretic synthesis of the composition of claim 2.

10. The composition of claim 2, wherein said combustible source is selected from the group consisting of MoO_3 + Zr + Si, WO_3 + Zr + Si and mixtures thereof.

11. An electrical heating element capable of being used at temperatures up to 1900°C comprising an integral article formed by micropyretic synthesis of the composition of claim 10.

12. The composition of claim 10 wherein said combustible source is between about 10 to 25 weight percent WO_3 + Zr + Si.

13. An electrical heating element capable of being used at temperatures up to 1900°C comprising an integral article formed by micropyretic synthesis of the composition of claim 12.

14. The composition of claim 1 comprising about 10 to 30 weight percent WSi_2, from about 0.5 weight percent to 4 weight percent SiC, from about 0.5 weight percent to 3 weight percent TiB_2, from about 0.5 weight percent to 3 weight percent HfB_2, up to 2 weight percent bentonite and up to 15ml per 30g of the above listed components, of colloidal silica.

15. An electrical heating element capable of being used at temperatures up to 1900°C comprising an integral article formed by micropyretic synthesis of the composition of claim 14.

16. The composition of claim 14 comprising 15-30 weight percent of WSi_2, 15-20 weight percent combustibles, 1-2 weight percent TiB_2 and HfB_2 and further comprising 0.5-1 weight percent C.

17. An electrical heating element capable of being used at temperatures up to 1900°C comprising an integral article formed by micropyretic synthesis of the composition of claim 16.

18. A pliable composition comprising by weight percent:

(a) between about 60 and 85% of a powdery mass of electrically conductive and/or semiconductive material selected from the group consisting of WSi_2, $MoSi_2$ and mixtures thereof;

(b) about 15% of WO_3 + Al + Si as a combustible source;

(c) about 2% of HfB_2 as a grain growth inhibitor;

(d) about 1 weight percent bentonite;

(e) about 3ml per 30g of the above listed components, of colloidal silica solution; and

(f) about 0.5 weight percent C.

19. An electrical heating element capable of being used at temperatures up to 1900°C comprising an integral article formed by micropyretic synthesis of the composition of claim 18.

20. A integral article formed by micropyretic synthesis of the composition of claim 1 for use as a gas ignitor.

21. An electrical heating element capable of being used at temperatures up to 1900°C formed by micropyretic synthesis of the composition of claim 1, said article comprising WSi_2, MoSi or a mixture thereof.

22. The composition of claim 1, further comprising additional combustion sources.

INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/US 95/06115

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C04B35/58 C04B35/65 H05B3/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C04B H05B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CERAM. ENG. SCI. PROC., vol.13, no.9-10, 1992 pages 596 - 604 C.H. HENAGER, JR. ET AL. 'Synthesis of composites in situ using displacement reactions' see abstract	5-9,20, 21
A	WO,A,93 14044 (UNIVERSITY OD CINCINNATI) 22 July 1993 cited in the application see claims 1-6,11,21; example T	1-22
A	EP,A,0 431 165 (INSTITUT STRUKTURNOI MAKROKINETIKI AKADEMII NAUK SSSR) 12 June 1991 see page 2, line 3-7; claim 1 see page 3, line 33-36	5-9,11, 20,21

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Information on patent family members

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